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PROGRESS IN THE LOS ALAMOS SCIENTIFIC LABORATORY
PROGRAM TO DEVELOP THERMOCHEMICAL PROCESSES
FOR HYDROGEN PRODUCTION*

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ABSTRACT

The Los Alamos Scientific Laboratory Program to develop thermochemical processes for hydrogen production is based on attempts to develop criteria required of an ideal process and to search for types of thermochemical cycles that approximate these criteria. The advantages of reactions with large entropy changes have been demonstrated. The necessity for experimental verification of conceptual cycles has become apparent from the program. This necessity has been stressed in the paper. It should be emphasized that any comparison of conceptual cycles or of engineering or cost analyses must eventually be based on real, rather than assumed, data.

INTRODUCTION

The inherent higher efficiency and potentially lower cost for the thermochemical production of hydrogen, versus the overall electrolysis path, is the motivation for the Los Alamos Scientific Laboratory program to investigate thermochemical processes for hydrogen production. The overall effort may be described as two complementary programs. The first is a program of basic research in thermochemistry and inorganic chemistry (together with reaction rate studies) for a large number of systems. The objective of this program is to synthesize (or recognize) optimized thermochemical cycles. This research includes the evaluation and comparison of the many processes proposed by other workers. The second general program is the application of results from the research program in more detailed studies of the "best" cycles with the objective of engineering practical, efficient and economically sound processes for thermochemical hydrogen production.

Up to the present time, most of the effort has been directed toward the identification, experimental verification and initial evaluation of chemical reaction cycles for water decomposition. From our own experience, and from an examination of proposed cycles published in the literature, it is apparent that hundreds of possible thermochemical cycles will eventually be conceived. From our own experience again, it is quite clear that most of these cycles (including those already published) will not merit serious consideration after even a modest program of experimental

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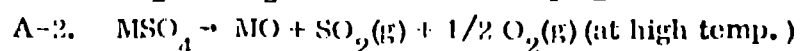
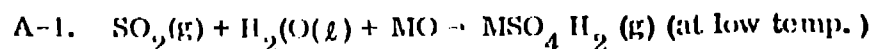
testing. Some of the cycles where reactions have actually been demonstrated do not meet the criteria required of an efficient and economic process. One can conclude, therefore that the development of an industrial technology for the thermochemical production of hydrogen will eventually require a large and comprehensive research and development effort. If this effort is to result in a practical new technology for hydrogen production it will be necessary to identify and develop processes that are optimized not only from the viewpoint of thermochemical efficiency, but also with respect to such requirements as: 1) cost of materials and chemicals; 2) materials of construction; 3) power requirements for the movement and separation of chemicals; and 4) heat exchangers and flow characteristics that permit efficient heat transfer at realistic power densities.

In our exploratory program, we are attempting to identify and test experimentally those processes that seem to approximate the criteria required for an ideal cycle. In an earlier paper [1] we considered the step-wise decomposition of water and concluded that specific values for the sum of the ΔS° terms and the sum of the ΔH° terms are required for the endothermic reactions of the cycle for maximum heat efficiencies in the process. These specific and related values depend on the temperature of the available process heat. These considerations also revealed the necessity for reactions with large entropy changes for cycles with a minimum number of reactions. We suggested the use of gaseous reactants in order to achieve large entropies of reaction. Some of the gaseous reactants we have considered are sulfur dioxide, sulfur trioxide, selenium dioxide, carbon dioxide, ammonia and the halogens.

Our recent and current studies of thermochemical cycles for water decomposition have been concerned primarily with reactions involving sulfates and halides. In the following sections, brief descriptions are given of the concepts that led to different potential cycles together with summaries of experimental results obtained during experimental evaluation of the cycles.

A. OXIDE-SULFATE CYCLES

These cycles are based on the observation that reactions of SO_3 (gas) with metal oxides to form metal sulfates, quite uniformly involve ΔS° values near -180 J/mol. K. Values for ΔH° vary widely and depend on the metal sulfate. Thus, the combination of this reaction with a reaction involving the addition of an oxygen atom to a metal or metal oxide can lead to successive or simultaneous reactions in which the combined ΔS° values are near -290 J/mol. K. This is near the ideal value derived for a heat source near 1150°K. Consequently, cycles based on this concept appear very attractive. The reaction cycle with water included as a reactant may be written as



Reaction A-2 is endothermic with typical ΔS^0 values near those required for maximum efficiency.

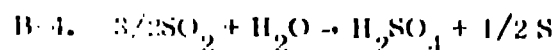
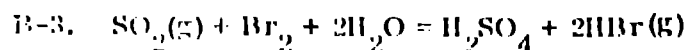
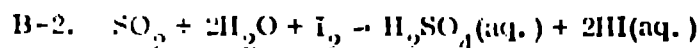
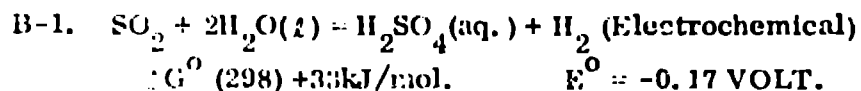
Many sulfates are known with decomposition temperatures suitable for reaction A-2 that are also sufficiently stable for reaction A-1 to be thermochemically possible. Among the least stable sulfates that might be useful in the cycle are zinc sulfate and cobalt sulfate. For these sulfates, reaction A-1 (with steam) is thermochemically favorable for temperatures below ~ 415 K. For reaction A-2, ΔH_R^0 (298) is +335 kJ/mol and the maximum possible thermochemical efficiency for the cycle (the net decomposition of water) is $\sim 85\%$.

It should be noted that reaction A-1 does not represent thermochemical equilibrium for the formation of sulfates which have practical decomposition temperatures. At equilibrium, sulfur plus the sulfate should be formed and one must be optimistic to assume the above reaction will actually occur even though it is a permitted reaction path. In our laboratory program, we have been unable to achieve reasonable rates for any of the permitted reactions in metal oxide, water and sulfur dioxide systems. This includes reactions to form the very stable sulfates (e.g. BaSO_4) where reaction A-1 does represent thermochemical equilibrium.

The unsuccessful attempts to develop oxide-sulfate cycles have been mentioned to illustrate the concept and also to show the thermochemical considerations of sulfate chemistry that led to conceptual cycles based on the formation and decomposition of sulfuric acid.

B. SULFURIC ACID CYCLES

In our experimental program, four different methods of sulfuric acid formation have been studied as shown in the following reactions.



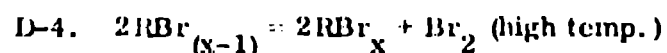
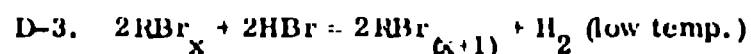
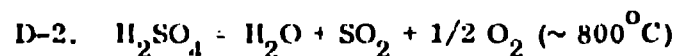
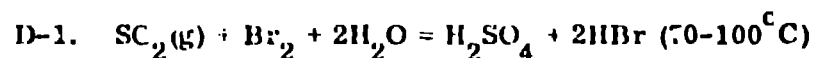
We have studied the decomposition of sulfuric acid and have found rapid and near equilibrium decomposition with suitable catalysts at high temperature (900-1200 K). The overall reaction appears to be a practical process for absorption of heat from a heat exchanger. Consequently, cycles involving sulfuric acid are of primary interest in our program.

C. HYBRID CYCLES

Two hybrid (thermochemical plus electrochemical) cycles were conceived and studied experimentally as part of the sulfuric acid work. One hybrid cycle is represented by reaction B-1 combined with the thermal decomposition of sulfuric acid. The second hybrid cycle is based on the electrolytic decomposition of the HBr formed in reaction B-3. The cycle concepts and some experimental data have been published previously [1,2] and will not be repeated here. From our work we concluded that such cycles might be feasible. However, it seems too early in the search for thermochemical cycles to abandon the potential additional advantages of the pure cycles in favor of hybrid cycles.

D. BROMIDE-SULFATE CYCLES

The only example of a bromide-sulfate cycle that we have studied is in reality a bromide-sulfuric acid cycle and is based on reaction B-3 above. The cycle concept may be illustrated as follows:



Conceptually, this is an attractive cycle since the sulfuric acid produced in reaction III-B-1 is quite concentrated and since the characteristic entropy changes for the addition of a bromine atom (from bromine gas) to a condensed phase are near the optimum value for reaction D-3 to occur at low temperature and reaction D-4 to also occur at temperatures near the sulfuric acid decomposition temperature. These features should permit a cycle with rather high heat efficiency. However, we have been unable to find reactants suitable for reactions D-3 and D-4 with reasonable rates for the low temperature reaction. Recently, the use of PdBr_2 catalysts has promoted more rapid reaction rates. Some of these results are being presented at this meeting [3].

E. SULFURIC ACID-SULFUR CYCLES

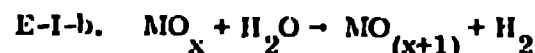
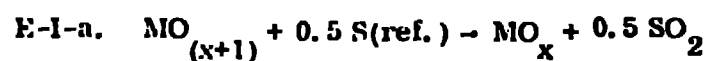
These cycles are based on reaction B-4 above, the formation of quite concentrated sulfuric acid and sulfur from sulfur dioxide and water at low temperature. This reaction represents thermochemical equilibrium in the system although reaction rates are very slow [4]. We are achieving some success in accelerating the reaction [5] and are currently studying a rather large number of cycle concepts based on the net reaction of sulfur with water to produce sulfur dioxide and

hydrogen. For illustrative purposes we have divided these concepts into two families of cycles each with several sub-classes.

E-I. Sulfuric Acid-Sulfur-Oxide Cycles

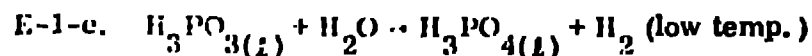
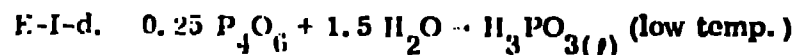
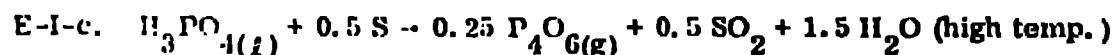
This family of cycles is based on an initial reaction in which sulfur reduces an oxide to a lower oxide or a metal. The different classes derive from alternative methods of closing the cycle.

Class 1. The basic reactions involve the reduction of an oxide with sulfur (at high temperature) to produce sulfur dioxide, followed by reaction of the reduced oxide with water (at low temperature) to produce hydrogen. The indicated reactions are:



For solid oxides, the cycle as written is not conceptually valid. For an entropy change typical of type I-b reactions (ΔS_b), the enthalpy change (ΔH_b) necessary for the reaction to occur, implies a ΔH_b value such that $T \cdot \Delta S_b$ (for typical ΔS_b values) will not equal ΔH_b at practical temperatures and reaction I-a would not occur. Therefore, some additional event with additional ΔS^0 is necessary. For this class of cycles, the additional ΔS is conceived to derive from the condition where the oxide $\text{MO}_{(x+1)}$ remains a condensed phase (solid or liquid) at high temperature and MO_x is a gaseous phase. In this case, the new typical ΔS_b value will permit the new reaction I-a to occur at temperatures that are well above the vaporization temperature of MO_x .

From data contained in the JANAF Tables, a I-a plus I-b type of reaction cycle involving phosphorous and phosphoric acids seemed thermochemically possible. Since the cycle involved only liquids and gases (above the melting of S), the cycle appeared to be attractive. The conceptual cycle may be written as follows:



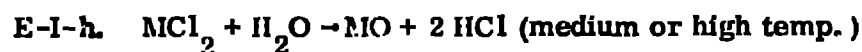
In contrast to the JANAF data, the heat of formation of P_4O_6 determined by Hartley and McCoubrey [6] indicated that reaction I-c could not occur. Therefore reactions I-c and I-e were tested experimentally. With palladium black as a catalyst, reaction I-e was conducted with some success. However, attempts to promote reaction I-c were unsuccessful.

Tests of reaction I-c involved heating sulfur as liquid and as vapor with phosphoric acid and with P_2O_5 (solid and liquid). Significant evolution of sulfur dioxide was not observed. Consequently, one can conclude that the heat of formation value for

P_4O_6 determined by Hartley and McCoubrey is accurate and that the value used for the JANAF Tables is greatly in error.

Additional potential reactants for the class 1 cycle have not been identified. A search for possible reactants is hampered by the lack of available thermochemical data.

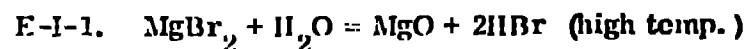
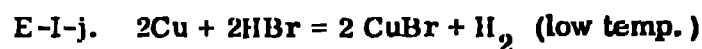
Class 2: The conceptual reactions involve the reduction of an oxide with sulfur to form a metal and sulfur dioxide, then the reaction of the metal with an acid (HCl or HBr) to form a metal halide and hydrogen, followed by hydrolysis of the halide to regenerate the oxide and the acid. The conceptual reactions are:



As indicated above, a reaction such as I-g is necessary for the production of hydrogen, since (for typical entropy charges) a metal that can be oxidized by water also forms an oxide that is too stable for the sulfur reduction reaction (I-f).

From a survey of the limited thermochemical data in the literature, it appears that a few reactants may be useful in the class 2 type of cycle. Experiments have not been performed.

Class 3. This type of cycle includes the I-g and I-f reactions shown above with the assumed difference that the metal halide produced in reaction I-g will not react directly with water and an additional step is used to effect the hydrolysis reaction. The following specific cycle illustrates the concept.

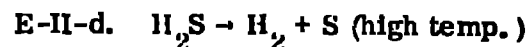
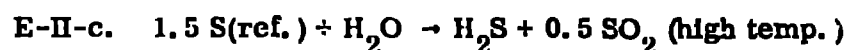
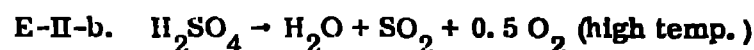
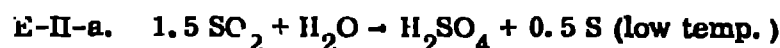


All of these reactions have been demonstrated in our experimental program. Reactions I-i and I-l are also used in industrial processes. Reaction I-k actually occurs in two steps. First to yield a concentrated solution of MgBr_2 that can be separated from the insoluble Cu_2O and second to remove water from the solution to yield $\text{MgBr}_{2(s)}$. The cycle has also been demonstrated with HCl substituted for HBr. Reaction I-j is more rapid with HBr. Other metals can be substituted for copper in this type of cycle. Substitution for Mg might also be possible.

E-II. Sulfuric Acid-Sulfur-Oxide Sulfide Cycles

The different families or classes of cycles under this heading include a reaction in which an oxide is reduced with sulfur to form a sulfide and the hydrogen production step involves the decomposition of H_2S .

Class 1. There is only one cycle in this class, however we have designated it as Class 1 because it is really the baseline process for the additional classes of cycles under the above heading. The reactions of this baseline cycle are:



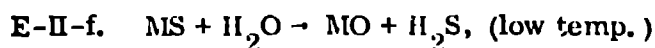
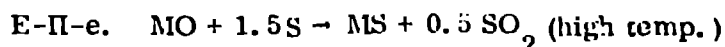
This baseline cycle has the very attractive characteristic that (above the melting point of S, 119 °C) only liquids and gases are involved. It is possible that this advantage will outweigh the obvious disadvantages. These are:

- (1) The free energy change (ΔG) is positive for both reactions II-c and II-d. Thus, work must be substituted for heat in these endothermic reactions.
- (2) Reactions II -c and II-d yield gaseous mixtures, in which the product gases are at significantly lower pressures than the reactants. Thus, additional work will be required to separate gases.

Since ΔG is positive for the two reactions, the thermochemical cycle, as written, is a combined heat plus work cycle and equilibrium constants for the reactions are less than unity at the maximum temperatures expected from practical heat sources. Whether or not the attractive features of the cycle can be realized will depend on actual yields achievable in reactions II-c and II-d and also on the development of methods to prevent excessive back reaction during cooling of reaction products. Methods for separating product gases will require development.

In our experimental program, all of the reactions of the baseline cycle have been studied and some success has been achieved in promoting possibly acceptable reaction rates and reaction yields [5].

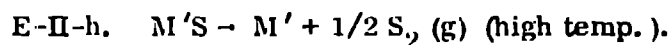
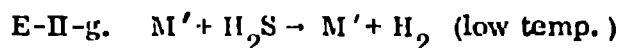
Class 2. The above basic cycle can be modified by inserting a two step cycle for reaction II-c. This would permit the use of reactions where ΔG values are negative and also simplify the separation of product gases. The reactions are as follows:



Class 2 cycles would include the thermal decomposition of H_2S as shown in reaction II-d above.

There appear to be several metals where the difference in stability between the metal oxide and metal sulfide is near the value required by the reproducible entropy changes associated with reactions of the II-e and II-f types. However, as indicated in reference [7], our most successful experiments have involved the use of CO_2 for reactions of the E-II-f type. Thus, a metal carbonate and H_2S are produced. The metal carbonate is then decomposed in a separate step.

Class 3. In class 3 cycles, reaction II-c of the basic cycle would be retained, but reaction II-d would be replaced by the two reaction cycle.



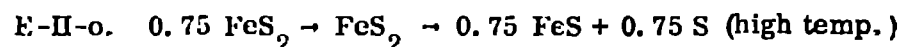
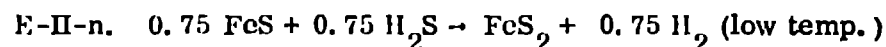
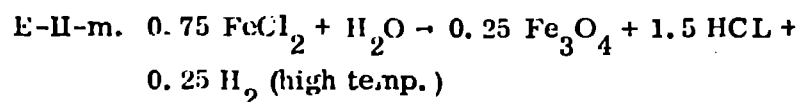
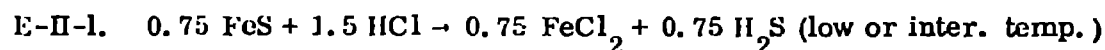
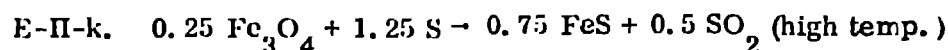
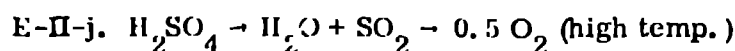
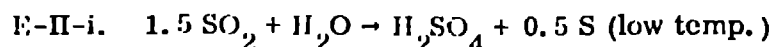
From literature data, there appear to be several metal-metal sulfide or sulfide-sulfide couples suitable for reactions II-g and II-h. However, attempts to conduct such reactions at reasonable rates have been unsuccessful. We have tested the couples: $\text{Bi-Bi}_2\text{S}_3$, NiS-NiS_2 and FeS-FeS_2 .

Class 4. Class 4 cycles would include both of the options described for the Class 2 and Class 3 cycles.

Class 5. In surveying the literature for reactants with thermochemical properties suitable for the Class 2 variation, it became apparent that there are many metal oxide-metal sulfide couples suitable for reaction II-e that will not undergo the hydrolysis shown as reaction II-f. In such cases, the sulfide could be reacted with an acid. The use of CO_2 described above is one example of this option. In a second variation, a stronger acid (HCl , for example) could be used to liberate the H_2S and the metal salt then hydrolyzed to recover the acid and regenerate the metal oxide.

If one recognizes the different options available to complete the overall cycle and also includes the different acids that might be used, one can divide Class 5 cycles into several additional cycle types. However, for the present, we will include these additional options under the Class 5 heading.

Since the verbal description of the Class 5 cycle is rather involved, it seems useful to depict the cycle with specific reactants for each of the steps. One of the possible cycles that we have conceived (including the sulfuric acid reactions) is the following:



This cycle is an example of how the number of reactions in a cycle can increase as one adds additional reactions to promote a difficult step in a potential cycle. At first glance certainly, there appear to be too many reaction steps for a credible cycle. Obviously we are not considering the cycle for practical use. However, in comparison to many cycles proposed in the literature, the cycle is actually advantageous. Most of the reactions will actually occur. In addition, since the type of reaction step is more important than the number, one can identify additional advantages for the cycle. These are:

- 1) The largest heat requirement for any process step is still the decomposition of liquid sulfuric acid.
- 2) There appear to be no difficult steps associated with the separation of gases.
- 3) High concentrations of HCl are not required.
- 4) There appears to be no necessity for the formation of solutions (and subsequent drying.)
- 5) The total heat requirement for all of the endothermic steps is sufficiently low so that a fairly high heat efficiency is theoretically possible.

From these considerations, it is possible to conclude that methods for the evaluation of cycles must be developed. We also wish to add that the most serious criticism of the cycle should be that it includes at least one reaction (E-II-n) that will not occur at a useful rate even though it is thermochemically possible.

F. ACKNOWLEDGEMENT

The conceptual cycles and experimental programs mentioned briefly in this paper

are the individual or joint work of Filmore F. Criss, Wesley M. Jones, John D. Farr, Caroline F. V. Mason, Edward I. Onstott, Charles L. Peterson and Willard G. Witteman. Details of the program will be described in papers by these investigators.

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